

Growth, characterization and dielectric property studies of gel grown barium succinate single crystals

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Abstract. Single crystals of barium succinate ($\text{BaC}_4\text{H}_4\text{O}_4$) were grown in silica gel medium using controlled chemical reaction method. Plate-like single crystals of size up to $3 \times 2 \times 0.2 \text{ mm}^3$ was obtained. Single crystal X-ray diffraction (XRD) studies confirmed that structure of the title compound is tetragonal. Powder X-ray diffraction (PXRD) pattern of the grown crystal and the Fourier transform infrared (FT-IR) spectrum in the range $400\text{--}4000 \text{ cm}^{-1}$ are recorded. The vibrational bands corresponding to different functional groups are assigned. Thermal stability of the grown crystals is confirmed by differential scanning calorimetry (DSC). Dielectric constant and dielectric loss have been calculated and discussed as a function of frequency at different temperatures.

Keywords. Barium succinate; gel growth; single crystals; dielectric constant; dielectric loss.

1. Introduction

Coordination molecular structures formed by the bridging of organic ligands with metal ions are found to exhibit a wide range of infinite zero-dimensional, one-dimensional, two-dimensional or three-dimensional frameworks with different interesting structural features. This structural diversity results from coordination bonding, hydrogen bonding, aromatic stacking interactions as well as Van der Waals forces. The keen interest of crystallographers in this field has resulted many interesting crystal structures with different electronic, magnetic and optical properties (Bao-Hui Ye *et al* 2005). The metal organic crystals are found to possess potential applications in catalysis, luminescence, gas adsorption and separation (Tanmoy Maity *et al* 2012). Extensive study on the crystallization and properties of metal dicarboxylates such as oxalates, tartrates and malonates are made by many investigators (Sahaya Shajan and Mahadevan 2004; Basharat Want *et al* 2007; Quasim *et al* 2009, 2010). However, studies on systematic growth and properties of metal succinates are very few in literature. Succinic acid is an organic dicarboxylic acid and each of the four terminal carboxyl oxygens in the succinate ligand can form coordinate bonds with central metal ions. The present work is to study the growth of barium succinate crystals in silica gel medium. In gel method, the gel acidified with succinic acids provides a controlled medium for the diffusion of supernatant cations into it, leading to the formation of

crystals. Gel medium provides a three-dimensional network in which the crystals are held in positions of their formations itself. Due to the unique advantage of suppression of nucleation centres in the gel medium, gel growth is a very effective technique for growing single crystals. Also defects found in gel grown crystals are less due to the absence of convection in the medium. Optimum conditions for the growth at ambient temperature were found by investigating different growth parameters. Single crystal X-ray diffraction studies have been conducted on the grown crystals to determine the unit cell parameters of the crystal. The grown crystals were also characterized by PXRD, FT-IR and DSC analyses. Result of electrical characterization of these crystals at different temperatures are also discussed.

2. Experimental

The single diffusion method was employed in the present study for the growth of barium succinate crystals. The chemicals used for the growth were AR grade succinic acid ($\text{C}_4\text{H}_6\text{O}_4$), barium chloride (BaCl_2) and sodium meta silicate (Na_2SiO_3). The crystallization apparatus consists of borosilicate glass test tubes of length 20 cm and diameter 2.5 cm. The growth process involves the diffusion of barium chloride solution into the succinic acid impregnated silica gel. The stock solution of desired specific gravity was prepared by dissolving appropriate quantity of sodium metasilicate powder in double-distilled water. Succinic acid solution of particular strength was taken in a beaker and the stock solution is added dropwise using a pipette. While adding the stock solution to the beaker

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containing succinic acid, continuous stirring is done to avoid the excessive local ion concentration which may otherwise cause premature local gelling and make the final medium inhomogeneous and turbid. The stock solution is added until the pH of the gel is set at the desired value. Test tubes were then tightly closed to prevent evaporation and contamination of the exposed surface of the gel by dust particles from the atmosphere. Depending upon the pH value of the gel, it is set after several hours. After ensuring proper gel setting, barium chloride solution of particular strength was slowly poured over the gel. The supernatant ions of Ba^{2+} slowly diffused into the gel medium where it reacts with the succinic acid and small crystals of barium succinate began to form within the gel. The systematic growth experiments were performed by adding BaCl_2 as feed solution of strength varying from 0.25 to 1 M over the set gel of pH range 4–6. The concentration of the succinic acid was varied from 0.25 to 1 M and the specific gravity of the gel was varied from 1.02 to 1.05 (Justin Raj *et al* 2007; Rajendran and Dale Keefe 2010; Mahalakshmi *et al* 2012).

After a growth period of four weeks, the crystals were harvested and the structural analyses were carried out. The single crystal X-ray diffraction data were collected using a Bruker AXS Kappa Apex 2CCD diffractometer, with graphite-monochromator $\text{MoK}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation. The unit cell dimensions were recorded at 293 K. Powder X-ray diffraction studies by Rigaku Miniflex $\text{CuK}\alpha$ monochromator of wavelength 1.541 \AA is also carried out to identify the planes of the grown crystals. FT-IR analysis of barium succinate crystals was done in KBr medium using powdered samples in the region from 400 to 4000 cm^{-1} using Jasco FT-IR 4100 spectrophotometer. DSC analysis was done employing Perkin Elmer DSC 4000.

Dielectric measurements on barium succinate single crystals as a function of frequency for various temperatures were carried out using LCR meter (LCR Hi TESTER 3532-50). The variation of dielectric constant (ϵ_r) as well as the dielectric loss ($\tan\delta$) of the crystal with frequency of applied field ranging from 100 Hz to 5 MHz is studied at different temperatures. The samples were finely ground and made in the form of pellets using a hydraulic press. The dielectric constant (ϵ_r) is calculated using the relation:

$$\epsilon_r = \frac{cd}{\epsilon_0 A}, \quad (1)$$

where C is the capacitance, d is the thickness and A is the area of cross section of pellet.

3. Results and discussion

3.1 Crystal growth

The supernatant solution, BaCl_2 diffuses into the gel column and reacts with succinic acid in the gel, producing the

necessary supersaturation for the slow precipitation of $\text{BaC}_4\text{H}_4\text{O}_4$. When the concentration of the diffusant is optimum, a few critical-sized nuclei are produced and due to the subsequent diffusion of BaCl_2 , crystals with definite faces and good sizes are formed. The habits of the crystals formed within the gel were leaf-like whereas at the gel solution interface small plates-like single crystals of good transparency were formed. The ideal growth conditions for developing almost defect-free crystals of barium succinate are optimized and summarized in table 1. The chemical reaction involved in the birth of a new phase and its subsequent development into a crystal is:



The experiment resulted in the formation of crystals of maximum size $3 \times 2 \times 0.2 \text{ mm}^3$. They were platy, colourless and transparent. The growth set up and the grown crystals of barium succinate are shown in figures 1 and 2, respectively.

3.2 X-ray diffraction studies

From the single crystal XRD studies, it is confirmed that the crystal structure of barium succinate is tetragonal. The measured cell parameters are: $a = 7.58 \text{ \AA}$, $b = 7.58 \text{ \AA}$, $c = 10.24 \text{ \AA}$, $V = 588 (\text{ \AA})^3$, $\alpha = \beta = \gamma = 90^\circ$.

These values are found to agree with the reported values (ICDD card no: 00-050-2415). The powder XRD

Table 1. Optimum conditions for growth of barium succinate single crystals.

Parameters	Optimum value
Gel density	1.03
pH	4.5
Concentration of $\text{C}_4\text{H}_6\text{O}_4$	1 M
Concentration of BaCl_2	1 M
Gel setting time	1 day
Growth period	4 weeks



Figure 1. Photograph showing crystal growth at different growing conditions.

diffractogram of barium succinate crystals are shown in figure 3. The d -spacing of different planes, the relative intensities of the observed peaks and FWHM data for each indexed plane are given in table 2.

3.3 FT-IR analysis

FT-IR spectrum of barium succinate at room temperature is shown in figure 4.

The characteristic absorption band at 1720 cm^{-1} is absent in the spectrum which assures that all the four oxygen atoms of succinic acid coordinates to barium atoms. The absorption bands at 2985 , 2957 and 2921 cm^{-1} can be assigned to asymmetric and symmetric C-H stretching vibrations of $-\text{CH}_2$ groups. The absorption band at 1546 cm^{-1} is due to asymmetric stretching vibrations due to COO^- group. The absorption band at 1449 cm^{-1} is due

to symmetric stretching vibration of COO^- group. The absorption bands at 1285 and 927 cm^{-1} are due to asymmetric and symmetric C-C stretching, respectively. The bending and rocking vibrations of COO^- are observed at 659 and

Table 2. PXRD data of barium succinate.

2θ	d (ang)	FWHM	hkl
14.5169	6.0968	0.2550	[101]
23.5834	3.7694	0.3263	[200]
23.9280	3.7159	0.3288	[112]
27.8035	3.2061	0.3553	[211]
28.3930	3.1409	0.3592	[103]
33.5962	2.6654	0.3924	[220]
34.5869	2.5913	0.3985	[004]
36.7713	2.4422	0.4117	[301]
41.6677	2.1658	0.4405	[312]
54.3809	1.6857	0.5118	[420]
67.4540	1.3873	0.5834	[521]
75.6225	1.2565	0.6290	[600]

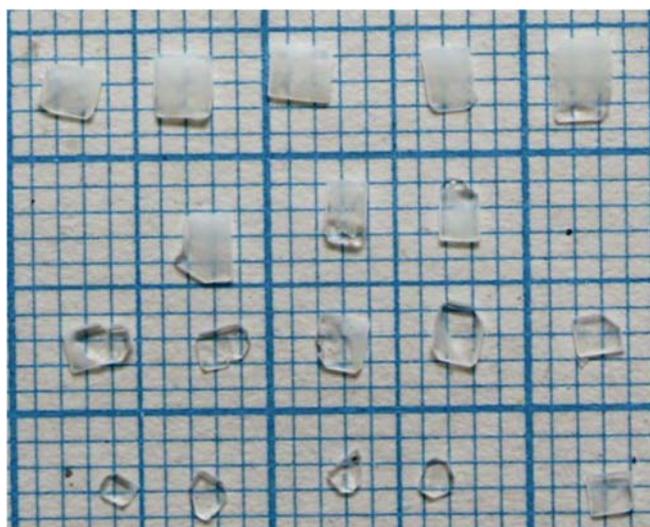


Figure 2. Grown crystals of barium succinate.

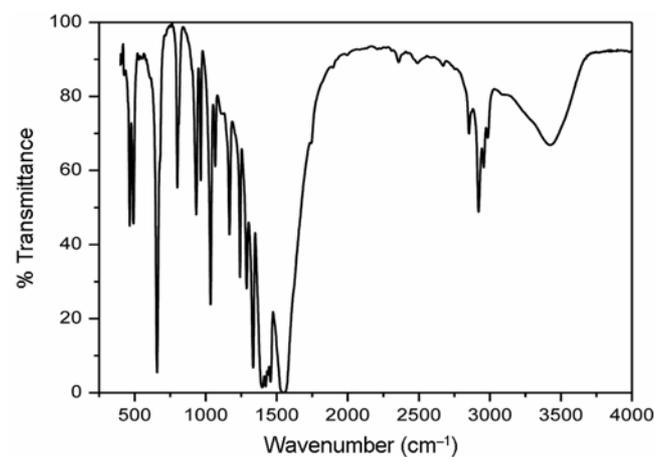


Figure 4. FT-IR spectrum of barium succinate.

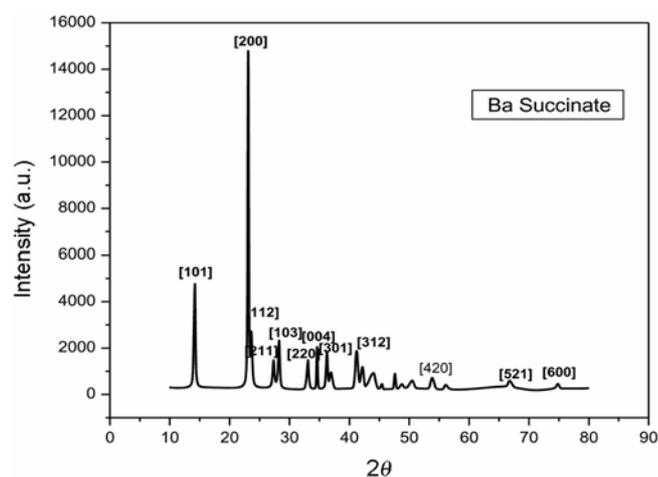


Figure 3. XRD pattern of barium succinate.

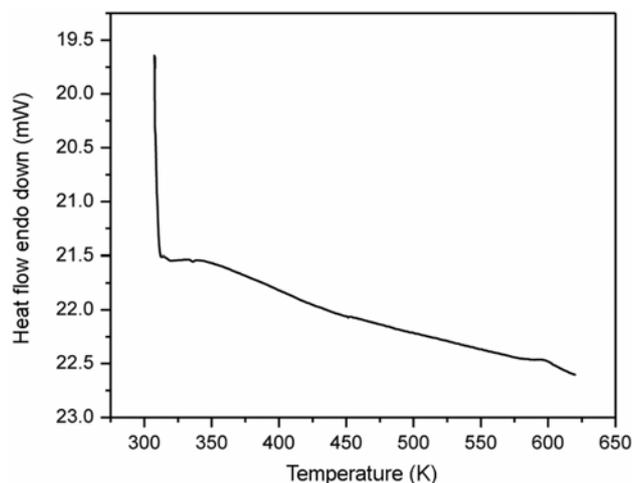


Figure 5. DSC spectrum of barium succinate.

523 cm^{-1} , respectively (Padmanabhan *et al* 2005; Jianguo Pan *et al* 2007; Krishnan *et al* 2007; Dhanya *et al* 2011).

3.4 Thermal characterization

Thermal characterization of the sample is carried out by the differential scanning calorimetry. The analysis was done with a heat flow from 323 to 648 K at 10 $^{\circ}\text{C}/\text{min}$. DSC curve of barium succinate crystal is shown in figure 5. The absence of any peak in this thermogram reveals that the compound is stable below 648 K, without any loss of weight.

3.5 Dielectric property studies

The variations of dielectric constant (ϵ_r) and dissipation factor ($\tan\delta$) with frequency of the applied field at

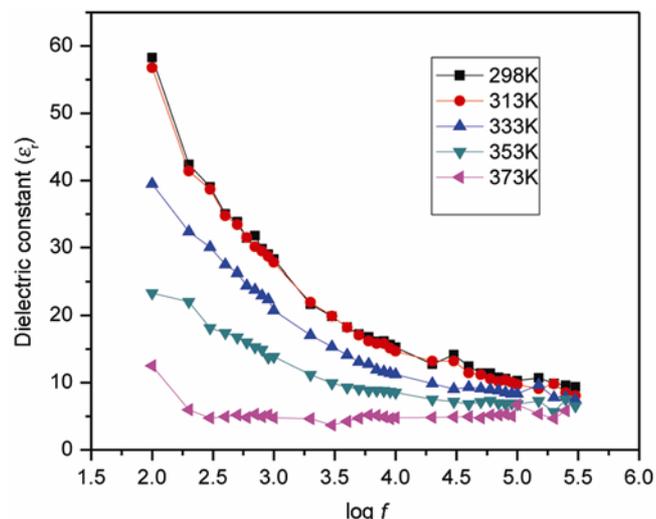


Figure 6. Variation of dielectric constant with frequency.

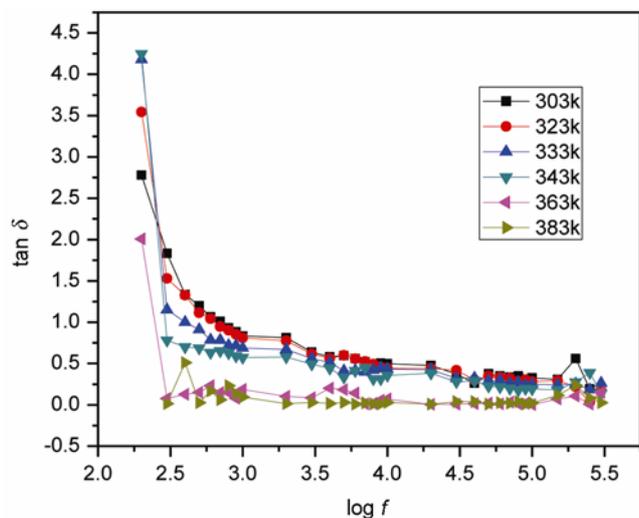


Figure 7. Variation of dielectric loss with frequency.

different temperatures are shown in figures 6 and 7 respectively. It is observed that the dielectric constant and dissipation factor decrease with increasing frequency and temperature. The low value of dielectric loss at high frequency suggests that the grown crystals possess good quality in terms of purity.

The four main contributions for polarization in a crystal are electronic, ionic, orientational and interfacial (and space charge). The electronic and ionic polarizations are due to the displacement of electrons and ions, respectively under an applied electric field and are temperature independent. The orientational polarization occurs due to the alignment of permanent dipoles which are otherwise randomly oriented; under the action of electric field. The interfacial polarization occurs when mobile charge carriers are obstructed by a physical barrier that inhibits charge migration. The charges get piled up at the barrier resulting into a localized polarization in the material. The interfacial polarization becomes effective in the low frequency range. Space charge polarization involves a limited transport of charge carriers until they are stopped at a potential barrier which could be a grain or phase boundary. Space charge and orientational polarization are relaxation processes and are strongly temperature dependent. The contribution towards polarization from space charge effects depends on purity and perfection of crystals, because the impurities or other forms of imperfection create potential barriers, limiting the transport of charge carriers and hence increasing the value of ϵ_r . The contribution from space charge towards polarization mechanism at lower temperature and higher frequency is insignificant as to make it negligible. However, as the temperature increases, the contribution from the space charge towards polarization may have a tendency to increase.

The dielectric constant is high at lower frequency region and decreases with increasing frequencies. This high value of dielectric constant at low frequencies is attributed to space charge and dipolar polarization. At lower range of frequencies dielectric constant decreases drastically, becoming a constant at larger frequencies. As the frequency increases, the dipoles do not comply with the varying external field. Therefore, the polarization decreases and hence, the dielectric constant decreases as the frequency increases. Also, in this case the decrease in dielectric constant with temperature is due to the effect of orientational polarization (Arora *et al* 2004; Gowri and Sahaya Shajan 2006; Firdous *et al* 2010; Abdurrahman Şengül *et al* 2012).

4. Conclusions

Barium succinate crystals were grown successfully by gel method and the optimum conditions of growth are achieved. From single crystal XRD studies crystal structure is determined to be tetragonal with lattice parameters

$a = 7.58 \text{ \AA}$, $b = 7.58 \text{ \AA}$ and $c = 10.24 \text{ \AA}$. The succinate phase formation was identified from the recorded FT-IR spectra and the band assignments were interpreted. DSC analysis depicted that the crystal is thermally stable up to 648 K. The dielectric constant is found to be decreasing with frequency, attaining a constant value at higher frequencies. Also the dielectric constant decreases with temperature. The dielectric loss is also found to be decreasing with frequency and temperature. The low dielectric loss at higher frequency of the sample indicates that title crystals possess lesser number of electrically active defects.

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